Poly(3,5-dichloroaniline) Doped with Different Sulfonic Acids

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Poly(3,5-dichloroaniline) Doped with Different Sulfonic Acids

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Poly(3,5-dichloroaniline) was prepared by chemical oxidation in the presence of various sulfonic acids as doping agent, using potassium permanganate as oxidant. 1-Naphtalene sulfonic acid, 2-naphatalene sulphonic acid, 1,5-naphtalene disulfonic acid, and p-toluenesulfonic acid were the acids of choice. Infrared and UV-Vis spectroscopy, utilized to characterize the polymers, revealed that the compounds exist in the emeraldine (conductive) oxidation state. The level of doping, conductivity, and morphology were determined as well. The presence of a sulfonic acid produces a morphological change, from granular to microtubule structures, which is responsible for the strong increase in the conductivity of the polymer.

Keywords: chemical oxidation; sulfonic acids; polymer conductivity; doping agent; potassium permanganate

1 Introduction

Polyaniline (PANI) has been extensively studied because, when doped with organic or inorganic acids, produces a highly conducting polymer (1). Polyanilines and their derivatives are materials with a wide range of applications (2). The stability, low-cost, ease of preparation, and the unique electrochemical properties make them very attractive for use in different fields: electrodes for rechargeable cells (3, 4), sensors and biosensors (5–7), corrosion passivation (8, 9), electronic devices (diodes, capacitors) (10, 11), etc.

Polyaniline has various oxidation states that consist, essentially, of alternate reduced and oxidized repeat units (12–14):

$$[(B\text{-}NH\text{-}B\text{-}NH)Y \ (\text{-}B\text{-}N{=}Q{=}N\text{-})1\text{-}Y]n \qquad (1)$$
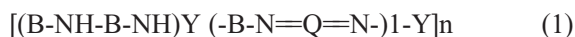
where, B = benzene ring; Q = quinoid ring.

The oxidation state of PANI is determined by the Y value. When Y = 0, the form is completely oxidized (pernigraniline), for Y = 1 the completely reduced form of the polymer (leucoemeraldine) exits, and when Y = 0,5 the polymer is in a half-oxidized state (emeraldine), that becomes conductive on acid doping. Each of these likely redox states may also exist in the doped polymer, but the actual conducting compound is that corresponding to the intermediate state, emeraldine.

PANI has been synthesized either by chemical or electrochemical means. Chemical synthesis in protic media has been accomplished using inorganic oxidizing agents, such as persulfate, dichromate, iodate, etc., in hydrochloric or sulfuric acid (15–17). More recently, large-size organic acids, such as camphor sulfonic, p-toluenesulfonic, fenilsulfonic, etc., have been employed (16–20). Even after comprehensive research, the mechanism of polymerization remains controversial. Although they disagree about the steps involved in the chain growing, several research groups accept a mechanism via cation-radical (21–24). To accept this statement, the work of Ding et al. can be quoted (25). Here, when a radical trap was utilized, inhibition of the polymerization process was observed, whereas in the presence of traps for the nitrenium ion (another proposed mechanism), PANI was obtained at a rate very close to that attained without the use of traps. A kinetic study carried out by Klavetter et al. in 1993 (26) established that the molecular weight of PANI, regardless the yield, remains constant after a time period, which is typical for chain polymerization reaction.

PANI is the only polymer that can be doped through two quite different processes: redox and acid doping. The acid doping is produced by protonation of the nitrogen atoms to yield a salt, e.g., protonated emeraldine, that once protonated, due to the instability of the quinoide-imine salt, undergoes relaxation to the benzenoid state through a proton-induced

mechanism of unshared spin (27, 28) that later on leads to structural changes, redistribution of charge, and the formation of a radical-cation per unit. In addition, half-filled polaron conducting bands are formed and, potentially, a metallic state may be attained where positive charges per repeat unit and an associate counter-ion exist.

It is also worth mentioning the results obtained in our laboratory (29) wherein various chlorinated polyanilines were prepared using selected oxidizing agents and sulfuric acid as dopant (with a very low level of doping, except those obtained with KMnO$_4$), as shown in Table 1.

In this paper, we report the chemical synthesis of 3,5-dichloroaniline in the presence of four selected sulfonic acids. The effect of these acids on the degree of doping, and the electrical conductivity of the polymers obtained (that is expected to be higher than the conductivity of the polymers in Table 1), were surveyed.

2   Experimental

All reagents were purchased from ALDRICH and were purified and/or recrystallized from ethanol/water (1:1).

Microtubules of poly(3,5-dichloroaniline), P(3,5-DCl), were prepared by chemical polymerization in the presence of the four selected sulfonic acids as dopant. Table 2 exhibits the acids utilized, their purity, and molar mass. These acids were selected based on previous studies related with the important effect of sulfonic group in obtaining microtubules (39).

The polymerization was conducted in a 0,015 M solution of the monomer, using acetonitrile/water (1:1 v/v) as solvent, at 50°C. Potassium permanganate (molar ratio aniline: KMnO$_4$ = 1:2) was used as oxidant. The molar ratio sulfonic acid:aniline was 2:1. The specific sulfonic acid and 3,5-dichloroaniline were dissolved in 200 mL of the CH$_3$CN/H$_2$O mixture and the resulting solution was heated to 50°C. The oxidizing agent (0,25 M) was slowly added with constant stirring. The stirred solution was remained at 50°C for 72 h. The product was filtered, washed thoroughly with deionized water, and methanol, and, finally, the precipitate was dried at 60°C in an oven.

To undope the polymers, they were treated with a 1:1 NH$_4$OH solution under strong stirring for 24 h. The product

Table 1.   Conductivity (σ,S $\cdot$ cm^{-1} $\times$ 1012) of di-chlorinated polyanilines synthesized with various oxidants, from reference (29)

Polymer	Oxidizing agent		
	ClO4-	Cr2O72-	MnO4-
Poly(2,5-dichloroaniline)	2,07	1,20	3230
Poly(2,3-dichloroaniline)	0,37	1,36	1620
Poly(3,5-dichloroaniline)	0,44	0,83	59900

Table 2.   Sulfonic acids employed as dopants

Acid	Purity in % m/m	M in (g $\cdot$ mol^{-1})
p-Toluenesulfonic (p-TS)	98	172
1-Naphtalene sulfonic (1-NS)	70	208
1,5-Naphtalene disulfonic (1,5-NS)	97	360
2,4-Dinitronaphtol-7-sulfonic (2,4-NS)	97	314

was then filtered, washed with water and methanol, and vacuum dried at 60°C.

The doping with iodine was performed by exposing the polymer to a gaseous atmosphere of iodine. The degree of doping was evaluated by measuring the increase in weight of the products.

The synthesized polymers were characterized by elemental analysis, on a Fison, Model EA-1108, Elemental Analyzer. Chlorine was quantified using the ASTM E-442 method (40).

The UV-Vis spectra were measured on a UV-3101 PC Shimadzu spectrophotometer, using Hellman QS-1000 quartz cells of 1 cm pathway. N-methyl-pyrrolidone was used as solvent.

FT-IR spectra of the undoped polymers were measured on a BRUKER, Model Vector 22, Spectrophotometer with KBr pellets.

The conductivity was measured by the conventional four-probe method on an Elchema Electrometer, using pellets of the pressed products (*ca*. 24000 Psi).

SEM images were obtained on a JEOL, Model 6400 F, High-resolution Scanning Electron Microscope (HR-SEM).

3   Results and Discussion

Poly(3,5-dichloroaniline)s were synthesized in the presence of the four selected sulfonic acids as dopant. The signals of the FT-IR spectra of the four polymers are very similar, evidencing analogy among the structures of all the substances, Figures 1 and 2. The more relevant signals were: a band at 3348–3256 cm^{-1} due to the N-H stretching; a band at 3060–3091 cm^{-1}, assigned to the aromatic C-H stretching; a band at 1501–1503 cm-1 due to the C=C stretching from aromatic diamine; a band at 1568–1570 cm^{-1} due to the C=C stretching from quinoidal diimine units; and, a band at 808–810 cm^{-1} ascribed to out-of-plane deformation of the aromatic C-H. Finally, the bands at 1045–1048 cm^{-1} and 670–671 cm^{-1}, were due to absorption of SO$_3^{2-}$ from the dopant (30).

The band assigned to C=C stretching due to benzenoid and quinoidal units, are very important in this kind of polymers since the ratio between the intensities of the two bands is an estimation of the degree of oxidation of the polymeric chain. Several workers have concluded that when the intensities of both bands are similar, the polymer is in its intermediate state, i.e., polyemeraldine (31).
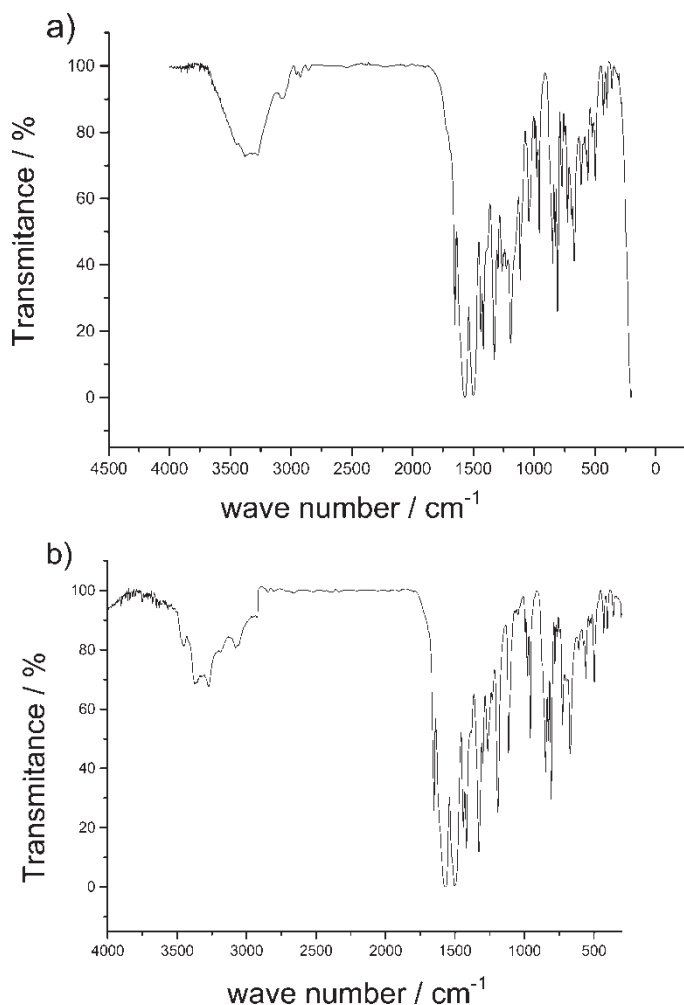
Fig. 1. P(3,5-DCl) FT-IR spectra obtained in the presence of: (a) p-TS acid; (b) 1-NS acid.

Fig. 2. P(3,5-DCl) FT-IR spectra obtained in the presence of: (a) 1,5-NS acid; (b) 2,4-NS acid.

The solubility of poly(3,5-dichloroaniline)s doped with the selected sulfonic acids was investigated in different solvents. Some solubility was observed in N-methylpyrrolidone, THF, and DMSO. An important parameter concerning the solubility of these polymers is the interaction of the solvent with the doping agent: the higher this interaction, the weaker the interaction between doped polymer chains, leading to a higher When p-Ts, 1-NS and 2-NS acid was employed as doping agent, no significant difference in the solubility of the polymers was observed in DMSO, however a lower solubility was obtained when 2,4-NS was used as dopant. Considering that 2,4-NS acid is the one containing more polar groups in its structure, it seems obvious that an increase in the polarity of the solvent should increase the solubility of the polymer doped with that acid. However, the results disagree with this explanation. The reason for such contradiction may be related to the considerable lower amount of dopant incorporated into the polymer, when the degree of doping is compared with other works, it brings about a lesser protonation of the nitrogen atoms of the quinoidal segments and,
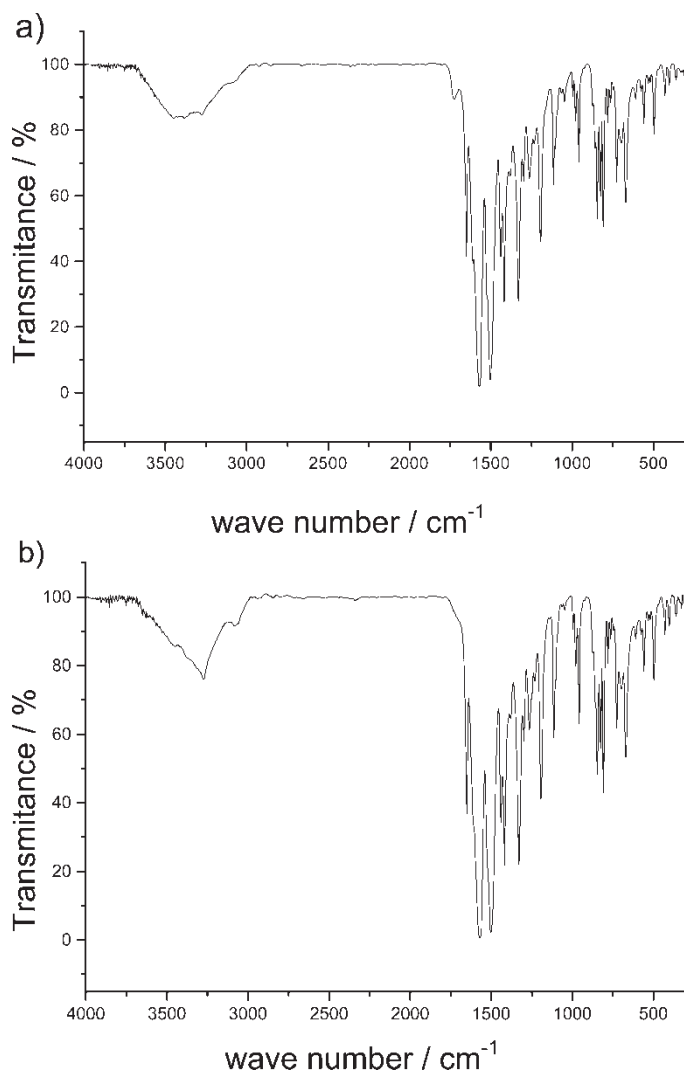
consequently, a lower interaction between the solvent and the doping acid in the polymer.

UV-Vis spectra of poly(3,5-dichloroaniline)s, synthesized using the selected sulfonic acids, were also measured using N-methylpyrrolidone as solvent, Figure 3. acids.

All the spectra are similar displaying bands at 270, near 360 nm ($\pi \rightarrow \pi$ transition of the benzenoid ring), and 600 nm (formation of an exciton of the quinoidal ring) (32, 33). When 2,4-NS was utilized, the exciton formation is nearly zero, which may be associated to the large molecular size of the acid, that leads to a low degree of doping and a poor formation of the polaron.

Table 3 lists the conductivity, degree of doping, and the wavelength of the corresponding polaron, obtained for the polymers doped with the selected sulfonic acid. It the size of the doping agent: the larger the doping agent, the larger the shift of the band. This is consistent with other workers' results (34, 35).
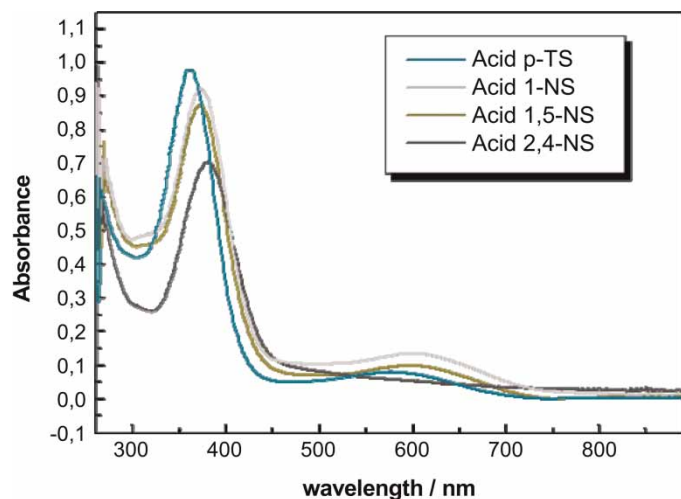
Fig. 3. P(3,5-DCl) UV-Vis spectra obtained in the presence of the four selected sulfonic.

For the sake of comparison, the spectrum of PANI, prepared under the same experimental conditions, (30) was run. The bands were now observed at 400 and 800 nm, respectively. Consequently, P(3,5-DCl) undergoes a hypsochromic shift ascribed to a decrease of conjugation along the polymeric chain owing to the presence of chlorine atoms in the aromatic rings. is noteworthy that the polaron position shifts toward larger wavelengths as a function of except for 2,4-NS acid, whose UV-Vis spectrum proves a very low level of doping and lack of the exciton, the conductivity of the P(3,5-DCl)s, synthesized in the selected sulfonic acid media, do not show significant differences.

When H_2SO_4 is substituted for the selected sulfonic acids as dopant, a decrease in conductivity was observed. In addition, the ratio of the benzenoid to quinoidal band intensities is almost unity, while with sulfuric acid the ratio was only 0.6, corresponding to a non-conductive oxidizing state (36). The electrical conductivity can be expressed as $\sigma = n \times e \times \mu$, where e, is the charge of the electron; n, the density of the charge carrier; and, μ, the mobility of the charge carrier (36), therefore, the conductivity of doped PANI may be dominated by n and μ instead of depending only on the degree of doping. This fact explains why,

Table 3. Electrical conductivity at room temperature, doping level (S/N), and exciton position of P(3,5-DCl)s synthesized in the presence of different sulfonic acids as dopants

Acid	Conductivity Undoped	$S \cdot cm-1$ Doped	Doping Level/S/N	Exciton/ nm
p-TS	$3,1 \cdot char\ 10^{-11}$	$4,2 \cdot char\ 10^{-7}$	0,32	580,50
1-NS	$2,2 \cdot char\ 10^{-11}$	$3,6 \cdot char\ 10^{-7}$	0,25	602,50
2-NS	$3,5 \cdot char\ 10^{-11}$	$4,0 \cdot char\ 10^{-7}$	0,27	602,50
2,4-NS	$1,1 \cdot char\ 10^{-11}$	$1,0 \cdot char\ 10^{-9}$	0,05	—
H_2SO_4	—	$6,0 \cdot char\ 10^{-9}$	0,34	570,00

despite the degree of doping being different in the three examples, their conductivities are roughly the same.

To corroborate the abovementioned findings, the 3,5-DCl polymers were studied using XPS, MEB, and solubility techniques. Figure 4 shows XPS (C1s and Cl2p) spectra of P(3,5-DCl) synthesized in the presence of p-TS acid in the undoped form. The spectra obtained in the presence of the other sulfonic acids are nearly identical.

The C1S signal is asymmetric and shows two shoulders indicating the existence of different kinds of carbon. Deconvolution was accomplished by taken the value of the well
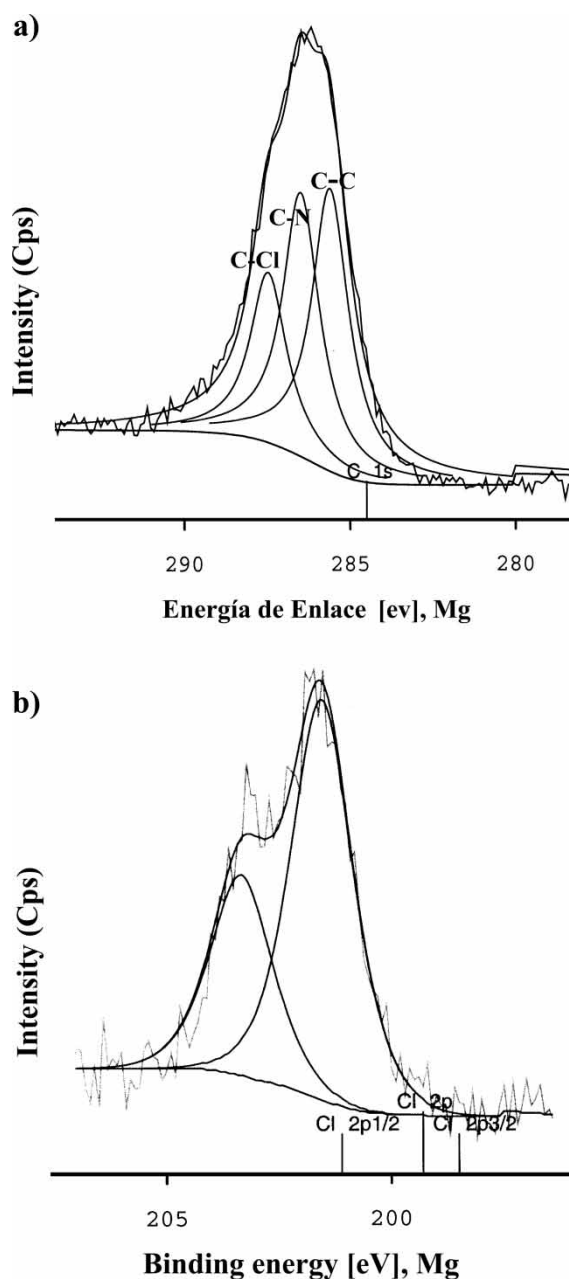

Fig. 4. XPS of P(3,5-DCl) doped with p-TS acid: (a) Cls; (b) Cl2p.

defined C-C bond as reference, bond energy 284,4 eV. These spectra showed a shift, ΔE, between 1,1 and 1,6 eV, consistent with the fact that the polymers were analyzed in their undoped state, which induce a charge effect. In this case, the signal of the C1S spectrum splits in three components. The more intensive peak, assigned to the C-C bond, was at 285,57 eV; the second, ascribed to the C-N bond, was at 286,45 eV, and the third, assigned to the C-Cl bond, was registered at 287,44 eV (37).

The Cl2p spectrum coincides with the typical spectrum of a C-Cl bond, corresponding to an aromatic ring, which appears as a doublet at 201,6 and 203,45 eV, respectively (28).
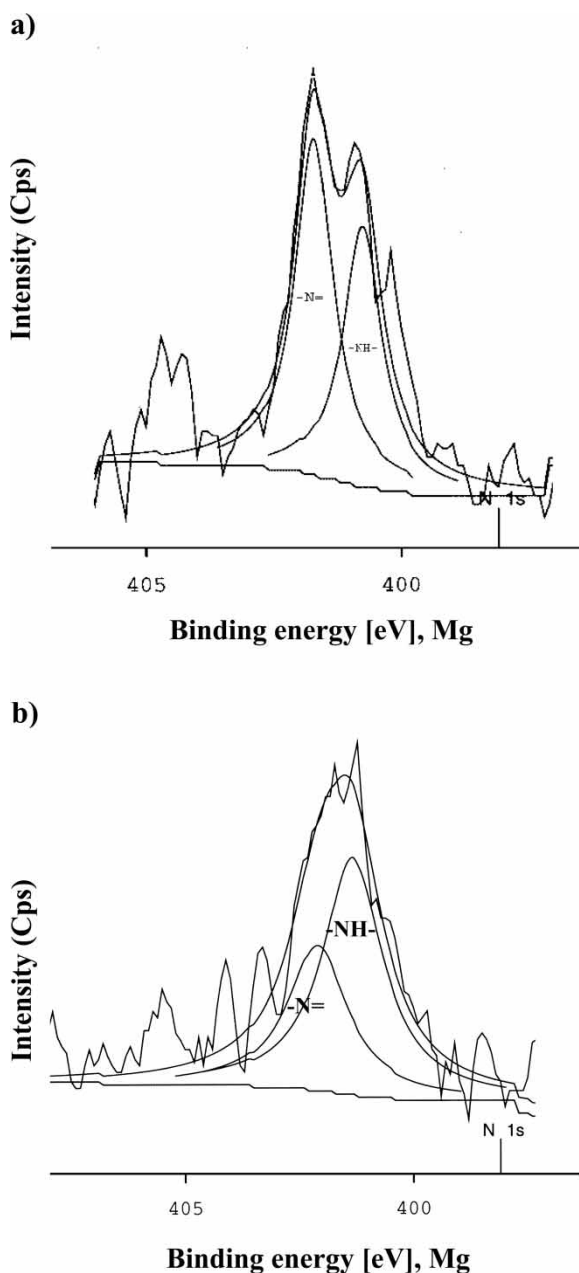
a)

b)

Fig. 5. P(3,5-DCl) N1s XPS doped with: (a) p-TS acid; (b) 1-NS acid.

Table 4.　Bond energy (eV) of P(3,5-DCl) doped with p-TS acid

Element	C1s			N1s		Cl2p
Specie	C-C	C-N	C-Cl	(-N=)	(-NH-)	Cl
	285,57	286,45	287,44	401,69	400,75	201,65
				(-N=)/(-NH-) = 1,3		203,45
ΔE (eV)	1,2					

Table 5.　Bond energy (eV) of P(3,5-DCl) doped with 1-NS acid

Element	C1s			N1s		Cl2p
Specie	C-C	C-N	C-Cl	(-N=)	(-NH-)	Cl
	285,85	286,24	287,29	402,09	401,32	201,82
				(-N=)/(-NH-)=1,5		203,62
ΔE (eV)	1,5					

The N1s spectrum is the more relevant in this case, because it can give information about the oxidation state of the polymer and the results can be compared with those obtained by FT-IR. As far as the polymers considered in the present work are concerned, in two of them (doped with p-TS and 1-NS) splitting in two signals is possible, as seen in Figure 5. The signal of the other two compounds was too narrow and could not decompose.

The first component was observed at 401,69 eV and was assigned to imine groups (-N=), while the second, located at 400,75 eV, was ascribed to amine groups (-NH-). However, the most relevant about these signals is the relationship of their areas. When decomposition took place, the ratio was 1,3 and 1,5, agreeing well with the results obtained by FT-IR, corroborating that the polymers are in their intermediate state. Tables 4–7 depict detailed information concerning

Table 6.　Bond energy (eV) of P(3,5-DCl) doped with 1,5-NS acid

Element	C1s			N1s	Cl2p
Specie	C-C	C-N	C-Cl		Cl
	285,71	286,45	287,44	401,40	201,52
					201,52
					203,32
ΔE (eV)	1,3				

Table 7.　Bond energy (eV) of P(3,5-DCl) doped with 2,4-NS acid

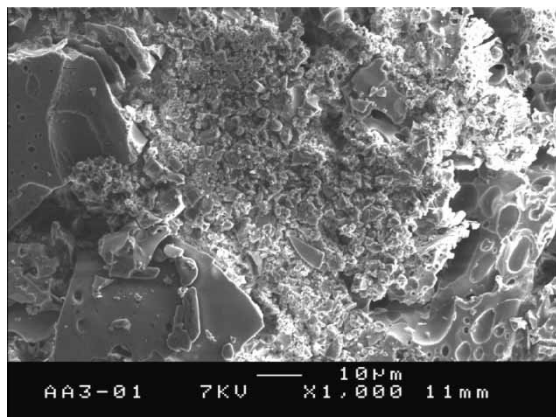| Element	C1s			N1s	Cl2p
Specie	C-C	C-N	C-Cl		Cl
	285,50	286,30	287,30	401,56	201,32
					203,42
ΔE (eV)	1,1				

Fig. 6. SEM micrograph of P(3,5-DCl) synthesized using p-TS acid as dopant.

to XPS spectra of the polymer synthesized in the presence of each of the sulfonic acids utilized.

As for the morphology, it was observed that formation of the microtubules is quite dependent on the sulfonic acid used as dopant. It has been found that the presence of a

naphthalenic ring in the sulfonic acid is a key requisite for microtubule formation (38).

Accordingly, the dopants employed in this work can be classified in two groups: the first includes p-toluenesulfonic acid, and the second, considers the number of sulfonic groups in the naphthalenic ring.

Figures 6 and 7 show micrographs of P(3,5-DCl) doped with p-toluenesulfonic acid, and 1-naphthalenesulfonic acid, respectively. A granular morphology was obtained in p-toluenesulfonic acid, whereas 1-naphthalenesulfonic acid produces small, non-orientated microtubules that, occasionally, join to form clusters of microtubules. Along with the micrograph of the polymer doped with 1-naphthalenesulfonic, an enlargement of the region is also presented, wherein the microtubules can be observed with more detail. 1,5-NS and 2,4-NS acids produce compounds of quite a different morphology. When the former acid is utilized, the polymer obtained shows a "wire-orientated" morphology, thinner than the microtubules obtained with1-naphthalenesulfonic. On the other hand, 2,4-NS gives rise to granular morphology, though in some regions incipient microtubules are observed (Figures 8 and 9).
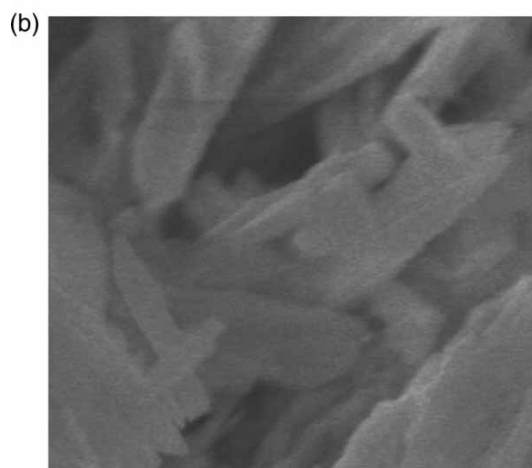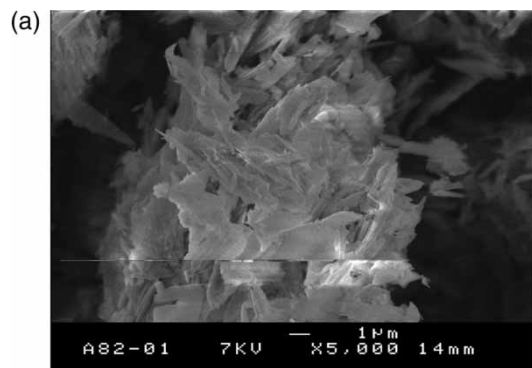

Fig. 7. SEM micrograph of P(3,5-DCl) synthesized using 1-NS acid as dopant (a); and, enlargement of the microtubules from the same micrograph (b).
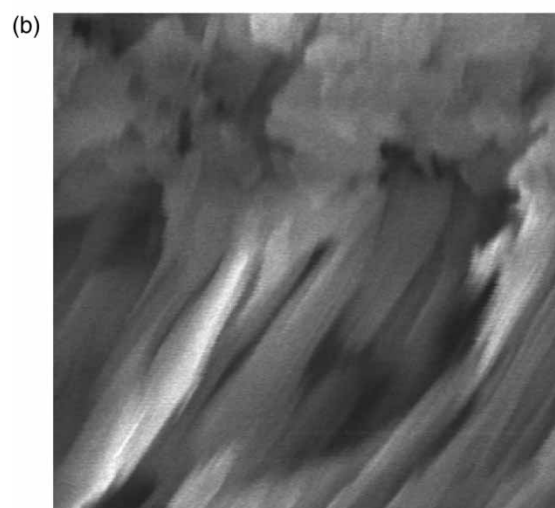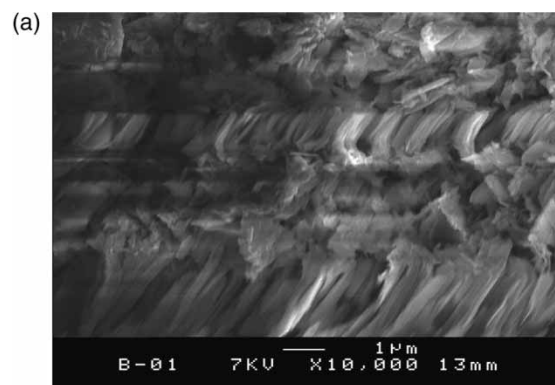

Fig. 8. SEM micrograph of P(3,5-DCl) synthesized using 1,5-NS acid as dopant (a); and, enlargement of the microtubules from the same micrograph (b).
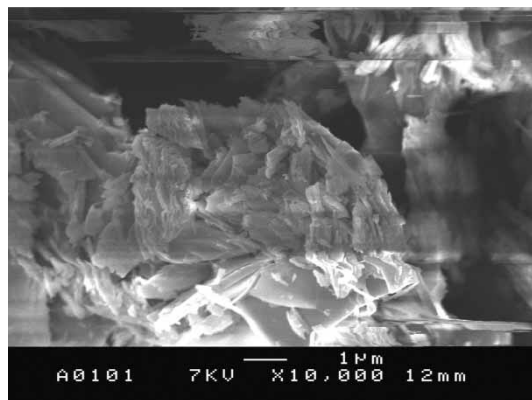
Fig. 9. SEM micrograph of P(3,5-DCl) synthesized using 2,4-NS acid as doping agent.

These results agree well with those of other workers, indicating that the presence of naphthalenic rings are essential for microtubules formation, whereas the number of sulfonic groups in the naphthalenic ring just brings about changes in the size, i.e., diameter and shape of the tubules.

As for the 2,4-NS acid, the low level of doping along with its large molecular size, may be the reason why microtubules were not obtained.

The assignment of an exact value to the diameter and length of the microtubules, on the other hand, is difficult because of the large number and to the proximity of them that hinders the measurements. Nevertheless, an estimation of such magnitudes indicates that the length ranges from 10 to 30 µm, while the diameter ranges from 0.1 to 1 µm. Finally, it can be concluded that the presence of sulfonic acid produce a strong increase in the conductivity of the polymer due to a morphological change, from granular to microtubule structure.

4 Conclusions

The presence of a sulfonic acid produces a morphological change, from granular to microtubule structures, which is responsible for the strong increase in the conductivity of the polymer.

5 Acknowledgements

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